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CODE OF SAFETY FOR CARBON DISULPHIDE (CARBON BISULPHIDE)

(Incorporating Amendment Nos. 1 & 2)

UDC 614.878 : 661.22

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Indian Standard

CODE OF SAFETY FOR CARBON DISULPHIDE (CARBON BISULPHIDE)

0. FOREWORD

0.1 This Indian Standard was adopted by the Indian Standards Institution on 25 May 1970, after the draft finalized by the Chemical Hazards Sectional Committee had been approved by the Chemical Division Council.

0.2 Carbon disulphide (carbon bisulphide) is a basic raw material for several chemical process industries including synthetic fibre and rubber. It is also used as a solvent for fats, resin, rubber, waxes, sulphur, selenium, bromine, iodine and phosphorus and as an aiding chemical in the manufacture of carbon tetrachloride, matches and pesticides. It is an extremely volatile, flammable and toxic liquid and may cause harmful effects, if not properly handled.

0.2.1 This standard attempts to guide the users and manufacturers in the recognition of hazards associated with carbon disulphide and in the recommended handling procedures. The information given should be used to the fullest extent and should be supplemented with additional information on design aspects of plant and equipment.

0.3 This standard is one of a series of Indian Standard codes of safety for hazardous chemicals.

0.4 This edition 1.2 incorporates Amendment No. 2 (December 2006). Side bar indicates modification of the text as the result of incorporation of the amendment. Amendment No. 1 had been incorporated earlier.

1. SCOPE

1.1 This code describes properties of carbon disulphide, the nature of hazards associated with it, and essential information on storage, handling, packing, labelling, disposal of waste, cleaning and repairs of containers, selection and training of personnel, personal protective equipment and first-aid.

1.1.1 This code does not deal with specification for design of buildings, chemical engineering plants, storage vessels and equipment for operations control and waste disposal.

2. TERMINOLOGY

2.1 For the purpose of this standard, the definitions given in IS : 4155-1966* shall apply.

3. PROPERTIES OF CARBON DISULPHIDE

3.1 Physical and Chemical Properties

a) Chemical names	Carbon disulphide, carbon bisulphide
b) Chemical formula	CS_2
c) Physical state	Extremely volatile, colourless, heavy liquid
d) Odour	Faint, sweet, ethereal odour when pure. Commercial grade has a strong characteristic odour
e) Relative density at 20°C/4°C	1.263 (water=1)
f) Vapour density	2.63 (air=1)
g) Boiling point at 760 mm Hg	46.3°C
h) Melting point	–108.6°C
j) Flash point (closed cup)	–30°C
k) Explosive limits	1.00 to 50.00 percent by volume in air
m) Ignition temperature	90°C
n) Solubility in water at 20°C	0.21g/100 ml
p) Refractive index at 20°C	1.627 6
q) Corrosivity	Commercial grades are slightly corrosive to some metals due to impurities
r) Vapour pressure at:	
10°C	198.1 mm Hg
20°C	297.5 mm Hg
30°C	432.76 mm Hg
40°C	616.7 mm Hg
s) Molecular weight	76.14
t) Odour threshold	0.21 ppm

4. HAZARDS ASSOCIATED WITH CARBON DISULPHIDE

4.1 Health Hazards

4.1.1 Carbon disulphide is harmful by inhalation of the vapour, prolonged or repeated contact of the liquid with the skin, or by oral intake.

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*Glossary of terms relating to chemical and radiation hazards and hazardous chemicals.

The threshold limit value (TLV) accepted at present for an eight-hour working day is 10 ppm by volume in air (60 mg/m^3).

NOTE — Threshold limit values are intended as guides in the control of hazards and should not be regarded as fine lines between safe and dangerous concentrations. They represent conditions within which it is felt that the workers may be repeatedly exposed, day after day, without their health being adversely affected.

4.1.2 *Toxic Effects from Inhalation*

a) *Acute poisoning* — Acute poisoning is rare. Sudden exposure to concentrations of about 1 200 ppm may produce headache, nausea, dizziness, and if prolonged, lead to circulatory collapse and unconsciousness. A concentration of 4 000 ppm may be fatal after an exposure period of half an hour to one hour. It may occur only by accident, such as equipment failure, and if workers enter enclosures or tanks without proper precautions.

b) *Chronic poisoning* — Chronic poisoning results from continued or freqently repeated exposure to relatively low concentrations of carbon disulphide. It probably occours only from inhalation of vapour and is insidious in development. The most serious forms result in acute mental disturbance, or in severe injury to the nervous system. It affects cardiovascular system, kidneys and liver.

4.1.3 *Toxic Effects from External Contact* — Carbon disulphide dissolves fat and may remove it from the skin, causing dryness and cracking, and producing sites for entry of harmful bacteria. Contact with the skin may cause only a temporary reddening and a burning sensation. If the liquid is not removed immediately, there may be extreme pain and later a more of less severe chemical burn.

4.1.4 *Toxic Effects After Oral Intake* — Poisoning by drinking carbon disulphide is rare. The signs are : loss of consciousness: ballor of the face, with blueness (cyanosis) of the lips; widening of the pupils; a rapid, feeble pulse; shivering; convulsions. If the quantity swallowed is not a fatal one, consciousness returns rapidly, but fatigue, dizziness and headache may last for days. Small quantities taken by mouth may cause vomiting, diarrhoea and headache.

4.2 Fire and Explosion Hazards — Carbon disulphide is a highly flammable volatile liquid with a low flash point, wide explosive range, and an extremely low ignition temperature (100°C). Contact with the surface of an ordinary electric light bulb will cause ignition. Carbon disulphide vapours, when mixed with air or oxygen in certain concentrations, are highly flammable and explosive.

4.2.1 The vapour is 2.63 times as heavy as air. It may travel some distance to a source of ignition, and flash back to the place of origin.

4.3 Incompatible — Carbon disulphide is incompatible with oxidizing agents, reducing agents, combustible materials, organic materials, alkali metals, halogens, metal oxides, metal azides, amines or imines and mercury fulminate.

5. STORAGE AND HANDLING

5.1 Storage

5.1.1 *General* — Due to high vapour pressure of carbon disulphide, bulk storage should always be under water and at or below atmospheric temperature. Tanks or drums should be sprayed with water in hot weather to keep the temperature low and the vapour pressure down.

5.1.2 *Type of Construction* — Structures in which carbon disulphide is stored should be non-combustible and either open type or well ventilated at floor level.

5.1.3 *Isolation* — Buildings for the storage of carbon disulphide should be isolated from other operations and buildings.

5.1.4 *Ventilation* — Carbon disulphide vapour is 2.63 times as heavy as air, therefore, special down draft or lateral type ventilation should be provided for room where carbon disulphide is stored or used. Although the threshold limit value for carbon disulphide is accepted as 20 ppm (*see* **4.1**) as an added precaution, the concentration of carbon disulphide vapour in the work room should be maintained below 15 ppm. Care should be taken to ensure that the same air is not recirculated in the room and the vapour is drawn away from the operators' faces. The ventilators of carbon disulphide storage rooms should be fitted with two layers of the fine wire mesh of non-corroding metal.

5.1.5 *Electrical Installations*

5.1.5.1 *Static electricity* — All carbon disulphide tanks, pipe lines, etc, should be connected by copper or aluminium strips and should be earthed to prevent fire due to static electricity.

5.1.5.2 *Motors and other electrical components* — Only flameproof motors should be installed in the areas where carbon disulphide is stored or used. Thermal cut-outs, switches, relays, transformers, etc, should not be installed in these areas. In case they are installed there or in a room which is not insulated by a perfect partition wall from the room where it is stored or used, they should be of flameproof type.

5.1.5.3 *Lighting and other electrical equipment* — All electrical lights, fittings and other electrical equipment, such as portable electrical hand lamps and tools, electric clocks, receptacles, panel boards used in the room where carbon disulphide is stored or used, should be flameproof. Extension cords of portable electrical equipment should be of three core, heavy duty type without any joints. Fixed lamps are preferred to portable extension lamps. Only approved safety flash lights (dry cell torches) should be used.

5.1.6 *Storage Tanks* — Carbon disulphide should preferably be stored in cylindrical tanks with dished ends. The tanks may be erected either vertically or horizontally. The carbon disulphide should be stored always under water in storage tanks. Carbon disulphide should not be filled in any vessel in excess of 85 percent of its capacity and 15 percent of tank volume should be filled with water. However, this may not apply to cases where carbon disulphide is stored in small containers of less than 250 litres capacity, provided such containers are provided with a vent pipe that is taken out of the building and the outlet is fitted with suitable flame arrester.

5.1.6.1 Tanks used for storage of carbon disulphide or the equipment in which carbon disulphide is used, should be kept properly closed and its inlet and outlet valves properly tightened in closed position when these tanks are kept empty; or else they should be kept filled with water or inert gas.

5.1.6.2 *Indoor storage* — Where the carbon disulphide is stored in containers not exceeding 250 litres capacity, it is not necessary to keep the container surrounded by a dike. No indoor storage tank should have a capacity exceeding 750 litres and the combined storage capacity of indoor storage tanks should not exceed 1 500 litres.

5.1.6.3 *Outdoor storage* — Any installation of storage tanks exceeding 1 500 litres should be of outdoor type with adequate clear distance between the installation and other buildings as follows:

Capacity of Installation	*Distance Recommended*
1 500 to 5 000 litres	6 metres
5 001 ,, 45 000 litres	10 metres
45 001 ,, 100 000 litres	13 metres
Exceeding 100 000 litres	15 metres

5.1.6.4 Where any indoor or outdoor storage installation of carbon disulphide exceeds 1 000 litres storage capacity, storage tanks should be surrounded by a dike, the total capacity of which is at least equal to the combined capacity of the tanks in it, plus 15 cm of height up to the bottom of dike overflow. The dike should be kept filled with water and the overflow should be sewered to a safe place. The water drain of the dike should be kept closed with a blind flange or valve which should be located outside or be capable of being operated from outside.

5.1.7 *Storage in Drums* — Carbon disulphide drums should be kept under cover with provision for cooling them. All the drums should be cooled with water before opening them, if they are exposed to sun.

5.1.7.1 Drums and other carbon disulphide containers should be filled and well flushed with cold and hot water before returning the empty drums for storage or before scrapping them.

5.2 Handling

5.2.1 Liquid carbon disulphide should never be pumped. Air pressure shall not be applied to containers of carbon disulphide because of the development of an explosive mixture. The chemical should be expelled from tank, drum or any other container by displacement with water pressure or inert gas pressure.

5.2.2 *Tools* — Only non-sparking, non-ferrous tools should be used in areas where carbon disulphide is stored or used and heavy blows should not be struck where carbon disulphide vapours are likely to be present.

5.2.3 Locomotives, boilers or diesel engines should not be permitted within 30 metres of the area around carbon disulphide storage tanks or usage points.

5.2.4 People handling carbon disulphide or working close to the storage or usage spots should wear rubber shoes or other shoes having sole fastened by sewing with string and not nails.

5.2.5 *Drains* — Drains provided for draining water, process fluids, etc, out of the plants using carbon disulphide should be closed drains or suitably covered trenches with adequate traps or sumps provided in the drains for trapping carbon disulphide carried over with the water or process fluid or process effluent. These traps should be checked for carbon disulphide contents which, if found, should be removed immediately and transferred to safe storage places.

5.2.6 *Pipelines* — Mild steel or alloy steel pipes should be used for transferring carbon disulphide.

5.2.6.1 All carbon disulphide pipes above 25 mm diameter should have flanged joints. For long runs of pipe lines, there should be minimum number of flanged joints to minimize chance of leakage. Screwed joints should be avoided. All outdoor carbon disulphide pipelines should be lagged suitably.

5.2.6.2 *Steam and other hot fluid lines* — Lagged or unlagged steam lines or any other hot fluid carrying lines which may produce surface temperature of 90°C should not be permitted in the area situated within a radius of 15 metres around carbon disulphide storage tanks or usage point.

6. TRANSPORTATION OF CARBON DISULPHIDE

6.1 General — Carbon disulphide shall be packed in standard containers when shipped by rail, water or highway and all precautions regarding loading, handling and labelling, shall be followed strictly.

Carbon disulphide shall not be offered for transportation by passenger trains.

6.1.1 No carbon disulphide should be allowed to escape into any sewer or drain during the loading and unloading from the transport vehicle.

6.1.2 Persons while on or attending to any vehicle conveying carbon disulphide should not smoke.

6.1.3 No fire or artificial lights capable of igniting flammable vapour should be allowed on any vehicle conveying carbon disulphide and no explosive substance or any substance or article capable of causing fire or explosion should be carried on such vehicle. This excludes the petroleum spirit or other fuel for use only in the propulsion of the vehicle.

6.1.4 A carbon dioxide or foam type fire extinguisher should be carried in an easily accessible position on any vehicle conveying carbon disulphide.

6.1.5 Every vehicle while engaged in conveyance of carbon disulphide should be constantly attended to by the driver or some other competent person of not less than 18 years of age.

6.1.6 All containers of carbon disulphide should be plainly marked 'FLAMMABLE LIQUID — KEEP FIRE AND OPEN FLAME AWAY'.

6.2 Transportation in Vehicles Other than Tankers — Carbon disulphide should not be conveyed on any vehicle unless it is packed as follows:

a) Glass or glazed earthenware containers stoppered and completely sealed, each containing not more than three litres of carbon disulphide, should be securely placed in a strong wooden case in saw dust, kieselguhr or other suitable material. Each bottle should be separated from any other by wooden partitions. The wooden case should not contain more than a total of 15 litres of carbon disulphide, or

b) Alternatively iron or mild steel container not exceeding 225 litres in capacity should be used. These should be maintained in good condition and should be securely closed so as to prevent leakage.

6.2.1 Carbon disulphide inside the drums should be kept covered under a layer of water (minimum 10 mm). Care should be taken to leave an empty an space of at least $7\frac{1}{2}$ percent of the capacity of the container over the combined volume of carbon disulphide and water.

6.2.2 Iron or steel containers should be carried on a vehicle with the bung uppermost. Each of the iron or steel container should be packed in a strong wooden perforated case or crate supported by wedges or choke blocks to prevent its rolling about.

6.2.3 Containers filled with carbon disulphide and cases containing bottles of carbon disulphide should not, during conveyance on any vehicle, be allowed to project beyond the sides or the back of the vehicle.

6.2.4 Except in a case where the vehicle has sides and a back of a height adequate to prevent the load from falling off during conveyance, the load should be securely fastened to the vehicle by some means such as ropes.

6.2.5 Each package with inside containers of three litres or larger capacity should carry a 'THIS SIDE UP' label. The package should preferably be provided with triangular top, forming an apex at the top.

6.3 Transportation in Road Tankers — Any road tanker used for conveyance should not carry more than 9 000 litres of carbon disulphide. No carbon disulphide shall be carried on any road tanker except in the carrying tank of the vehicle.

6.3.1 During the operation of filling or emptying the carrying tank of a road tanker, the vehicle should be constantly attended to by the driver thereof or by some other competent person of not less than 18 years of age.

6.3.2 The engine of the road tanker vehicle should be stopped during the whole period of the operation of filling or emptying and should not be run until the carrying tank of the road tanker and any tank in which carbon disulphide is being delivered or from which any carbon disulphide is being taken out have been securely closed.

6.3.3 Adequate provision should be made to prevent the accumulation of a dangerous static charge of electricity by properly earthing the carrying tank during the operation of filling and emptying the tank.

6.3.4 Whenever carbon disulphide is being discharged from a road tanker, care should be taken to see that the vessel or container that is being filled also is satisfactorily earthed.

6.3.5 Carbon disulphide filled in the carrying tank of the road tanker should be kept covered under a layer of water and vapour space of at least 6 percent of the capacity of the tank should be left empty.

7. LABELLING

7.1 All containers (including tank cars) of carbon disulphide shall bear the label given in Fig. 3 of IS : 1260-1958*. The lower half of the label shall have the following words printed in red letter. Any other label or warning or statement required by statutes, regulations or ordinance may also be used in combination or separately.

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*Code of symbols for labelling of dangerous goods.

CARBON DISULPHIDE
DANGER ! EXTREMELY FLAMMABLE,
VAPOUR HARMFUL, HIGHLY VOLATILE

Keep away from fire, sparks, or heated surfaces. Store in a cool place and keep container closed. Use only with adequate ventilation.

Avoid breathing vapour.

Avoid contact with skin and eyes.

8. PREVENTIVE MEASURES

8.1 General

8.1.1 Operation in which carbon disulphide is used should be completely enclosed both because of its high toxicity and fire hazard.

8.1.2 Carbon disulphide should be kept in approved type of safety cans if it is often required for use in small quantities. Open handling of carbon disulphide should be avoided.

8.1.3 Persons who are likely to get exposed to unknown concentrations of carbon disulphide vapours should wear special type of personal protective equipment, such as canister type gas mask, self contained breathing equipment, safety belt, etc, requirement of which may be assessed according to the prevailing working conditions.

8.1.4 A readily accessible, well marked safety shower, controlled by a quick opening valve, should be located in each area where carbon disulphide is handled; small hose line connected to a clean water line and bubbler drinking fountain for washing the eyes should also be provided.

8.1.5 Smoking and carrying out of hot job involving heating, open flame or spark should be prohibited in the area situated within a radius of 15 metres around the place of bulk storage or usage of carbon disulphide and suitable sign boards indicating 'Highly flammable, No naked flame — No spark — No smoking — No welding zone' should be conspicuously exhibited in these areas.

8.1.5.1 The jobs involving use of welding and gas cutting sets and blow lamps in the prohibited area may be carried out under the supervision of a trained and responsible person after taking all the adequate safety precautions and after obtaining the necessary authorization from the fire or safety officer.

8.2 Spills and Leakage

8.2.1 Rope off and clear the area. Post warning signs, and watchers provided with adequate personal protective equipment. Keep all sources of ignition away. Allow the spilled carbon disulphide to evaporate. Steps should be taken to ventilate the area as quickly as possible

8.2.2 If spilled or splashed on the body, remove immediately any clothing, gloves or shoes soaked with carbon disulphide and wash the body thoroughly.

8.3 Employee Education and Training

8.3.1 Safety in handling carbon disulphide depends upon the effectiveness of employee education, training and supervision.

8.3.2 The education and training of the employees to work safely and use the personal protective equipment or other safeguards, is a responsibility of supervision.

8.3.3 Employee education and training should emphasize the need of handling carbon disulphide according to methods outlined in this standard.

8.3.4 Before being placed on the job, new employees should be instructed thoroughly in the hazards of handling carbon disulphide. Older employees should be reinstructed periodically.

8.3.5 Each employee should know the location, purpose, use, and maintenance of personal protective equipment. Each should also be taught when and how to use this equipment and be trained in its use.

8.3.6 Each employee should know the location of safety showers, bubbler drinking fountains and hose lines.

8.3.7 Only intelligent, dependable and properly trained employees should be given the responsibility of operating valves which control the movement of carbon disulphide to and from storage tanks, tank cars, and containers.

8.3.8 Employees should be trained to report to the proper authority all suspected leaks or equipment failures, and any signs of illness or skin irritations.

8.3.9 Each employee should be trained in the emergency and first-aid measures, and should realize the necessity of prompt application of first-aid in case of contact with carbon disulphide or exposure to the vapour.

8.3.10 Each employee should be taught the importance of proper personal habits as protection against carbon disulphide illness.

8.4 Preplacement Physical Examination — Careful preplacement physical examinations should be made on all men who are to work with carbon disulphide. Certain individuals, who might be susceptible to the action of carbon disulphide, should not be assigned to operations involving its use. Exposure should be absolutely prohibited to:

a) alcholics;
b) those with a history of gastro-intestinal disorders, abnormal blood pressure (high or low), peripheral vascular diseases or neurological diseases of any type; and
c) those with a history of abnormal behaviour or impaired mentality.

8.5 Periodic Medical Examination — Workers exposed to carbon disulphide should be examined frequently, preferably every 3 or 4 months by a physician acquainted with the hazards involved. The periodic examination should include standardized measurements of blood pressure; simple observations of the reflexes and queries as to the symptoms indicating poisoning. The occurrence of abnormal blood pressure readings or reflexes, or of the symptoms of chronic carbon disulphide poisoning should lead at once to examination of the place of work, the manner in which the affected man performs his work, and his medical condition as compared with fellow workers in the same occupational group. Consideration should be given to at least temporary shifting of affected employees to work free from exposure to carbon disulphide.

8.5.1 A rotating schedule should be set up for workers exposed to carbon disulphide so that periods of exposure are followed by periods, at least as long, of work in the uncontaminated air.

8.6 Personal Protective Equipment

8.6.1 *General* — Personal protective equipment is not an adequate substitute for safe working conditions and carefulness on the part of individual employees. Furthermore, if personal protective equipment is to be used effectively, each worker should be fully informed with respect to its proper employment, and should be trained in its use.

8.6.2 *Respiratory Equipment* — All respiratory equipment should be approved by the concerned authority for the use to which it is to be put and should be used in strict compliance with the instructions issued by the manufacturer.

8.6.2.1 *Low concentrations of vapour : brief exposure* — Suitable respiratory protection is needed if even small concentrations of carbon disulphide vapour are to be encountered. For concentrations of vapour not exceeding 2 percent by volume, and for relatively brief exposure periods, an industrial respirator with full face mask and canister may be used, provided also that the oxygen content of the air is not less than 16 percent by volume. Such respirators should be readily available at all points where such limited exposures occur. They are not suitable for emergency, since, in emergency, the actual carbon disulphide concentration is unknown.

8.6.2.2 *High concentrations of vapour : prolonged exposure : emergencies* — Where the vapour concentration exceeds 2 percent by volume, or is unknown, as in most emergency situations, or when the oxygen content of the atmosphere is below 16 percent by volume, or when exposure is prolonged, supplied-air respiratory equipment of appropriate design with full face masks, should be used by all persons entering the contaminated area. This is true also for oxygen-deficient atmospheres, such as those which exist frequently in storage tanks, tank cars, pits and sewers handling carbon disulphide waste. Such supplied-air respirators include:

a) hose masks with or without air pump, as may be required to maintain an adequate air supply (hose inlet shall be in a vapour-free atmosphere);
b) air line masks with compressed air supply, equipped with a suitable filter and a proper reducing valve or other device designed to effect delivery of air to the piece under optimum pressure (*see* Note); and
c) self-contained breathing apparatus with proper reducing valve and filter, containing an adequate supply of stored oxygen or air (such equipment allow greater mobility but usually requires more training for its proper employment).

NOTE — Hose or air line masks are suitable for use only where conditions will permit safe escape in case of failure of the air supply.

8.6.2.3 *Inspections* — Gas masks and other respiratory protective equipment should be inspected at regular intervals and should be cleaned and serviced after each use. It is particularly important that canisters and oxygen cylinders be replaced before they become exhausted.

8.6.3 *Rescue Harness* — A safety belt and life-line should be used in every case where the wearer of respiratory equipment enters a confined atmosphere. A man should be stationed outside the contaminated area to act in case of an emergency; this attendent should also be provided with adequate protective equipment in case it becomes necessary for him to enter the contaminated area.

8.6.4 *Skin Protection* — To prevent injury to the hands of workers exposed to liquid carbon disulphide or to carbon disulphide solutions, gloves used should be impervious to this chemical product. If rubber gloves are a necessity, the ones selected should have the greatest resistance to carbon disulphide. The hands should be coated with a salve, and a thin cotton glove worn directly over this salve and beneath the rubber gloves. Gloves should be washed daily. Rubber gloves should be washed inside and out, and thoroughly aired and dried to remove the carbon disulphide.

8.6.5 *Eye Protection* — To prevent injury to the eyes, suitable safety-goggles should be used by persons exposed to high concentrations of vapour or liquid.

8.7 Fire Fighting — In case of fire, it is best to use foam or carbon dioxide extinguishers. A hose stream should not be used because it would scatter the liquid and might spread flames.

8.7.1 In case of big fires, hydrant water hose with fog nozzle, foam making branches or foam generating nozzles may be used.

8.7.2 While attending the indoor fires, suitable type of gas masks or special type of respiratory protective equipment shall be used by the persons concerned.

9. AIR ANALYSIS

9.1 To keep the concentration of carbon disulphide within desired limits, it is necessary to sample the air at frequent intervals and determine its carbon disulphide content. Proper measures should be taken immediately if the concentration exceeds specified limits.

9.1.1 Both calorimetric and volumetric methods for determination of carbon disulphide vapour in air are described in detail in Appendix A.

10. FIRST AID

10.1 Acute Poisoning by Inhalation — Remove the patient promptly from the contaminated atmosphere. If breathing has stopped, give artificial respiration by the prone pressure or the rocking method. If oxygen is available and any one familiar with oxygen inhalation apparatus is present, give oxygen. Attempts to give oxygen by one not familiar with the apparatus may cause loss of valuable time or actually harm the patient. Keep the patient comfortably warm. Call a physician as soon as possible.

10.2 Chronic Poisoning — Chronic poisoning may produce sudden hysteria or violent behaviour. If necessary, tie the patient's arms and legs to prevent him from injuring himself and others. Call a physician at once. A patient suffering from psychic disturbance due to carbon disulphide exposure should always be hospitalized.

10.3 Skin Contact — Remove contaminated clothing and do not allow the patient to wear it until it is thoroughly aired and freed from carbon disulphide. Wash skin thoroughly with plenty of water.

10.4 Contact with Eyes — If liquid carbon disulphide is splashed into the eyes, they should be washed promptly for at least 15 minutes with copious quantities of water. Medical attention should be obtained.

10.5 Ingestion — If a worker has swallowed carbon disulphide and is conscious, he should be made to vomit by drinking a glassful of lukewarm salty water, or soapy warm water. If necessary, the patient should be encouraged to stick his finger down his throat to induce vomiting. Repeat this procedure at least three times. Call a physician promptly.

11. CLEANING AND REPAIRS

11.1 The hazardous nature of tank inspection, cleaning, or repairs requires that the foreman and crew be selected, trained, and drilled carefully. They should be fully familiar with the hazards, and the safeguards necessary for the safe performance of the work.

11.2 Wherever possible, enclosures should be cleaned from the outside, using clean-out door.

11.3 All pipelines into or out of the tank or other apparatus should be disconnected, preferably by removing a complete small section. Valves, cocks and blank flanges should not be relied upon.

11.4 Danger signs should be placed suitably to indicate when workmen are in the tank or other apparatus.

11.5 Be sure that the tank may be left by the original entrance.

11.6 Lock all electrical switches in the off position, remove belts and completely safeguard against accidental starting of any agitating equipment or other moving parts located inside or adjacent to the tank entrance.

11.7 Before entering a tank, and during the course of the work, tests should be conducted by a qualified person to determine if further washing is necessary and to make sure that there is no oxygen deficiency, and that no harmful gases are present. Before directing men to enter a tank, an inspection of the interior should be made by the foreman, equipped with a hose-type gas mask, life belt, and life line; another person should be on guard during the inspection.

11.8 One man on the outside of the tank should keep the men in the tank under constant observation, and at least two men should be available to aid in rescue if any of the men inthe tank are overcome.

11.9 A supplied air respirator or self-contained breathing apparatus, together with rescue harness and life line should always be located outside the tank entrance for rescue purposes, regardless of the type of respiratory equipment or air supply which is provided for employees inside the tank.

11.10 In addition to protecting the workmen actually engaged in cleaning and repairing the tank, attention should be paid to the protection of workers in nearby areas.

11.11 Cleaning or making repairs inside a tank may be hazardous even though the tank contained a non-toxic, non-flammable material. In addition to the precautions generally recommended for tank work, such as those mentioned earlier, additional precautions are recommended as follows:

a) Drain the tank as completely as possible.
b) Wash the interior of the tank thoroughly with running water and allow it to drain.
c) Since carbon disulphide is frequently absorbed by scale in the inside of storage tanks and is not removed by flushing with water or by simple aeration, the carbon disulphide should be boiled out carefully. The recommended practice, after the tank is drained, is to flush several times with water, fill the tank completely with water and then slowly raise the temperature by the addition of hot water. The manhole cover should be left open during this heating process and the water in all parts of the tank should be agitated occasionally to ensure uniform distribution of the heat. This heating-up process should be carried out gradually and cautiously to avoid any possible sudden evolution of carbon disulphide vapour when the temperature of the water reaches the boiling point of carbon disulphide. Water in the tank should be brought to 100°C and held at that temperatures so that it is actively boiling for several hours before it can be assumed that all carbon disulphide has been driven off. Those not completely familiar with this process should consult the carbon disulphide supplier.
d) Direct a stream of fresh air into the tank and ventilate until all traces of carbon disulphide have been completely evaporated and purged from the tank. It is good practice to keep a stream of fresh air flowing through the tank during the entire period someone is in it, regardless of the type of respiratory equipment that is used.

12. WASTE DISPOSAL

12.1 Small quantities of liquid waste, such as is usually produced in laboratories, should be kept under water in an approved type safety can.

12.2 Waste carbon disulphide may be burned in a remote location if proper open containers are supplled and provision made for lighting with a train from the windward side, or a remote control lighting device is used. It will evaporate rapidly if poured on the ground at a safe location.

12.3 Under no condition should waste be flushed down the sewers.

APPENDIX A

(*Clause* 9.1.1)

METHODS FOR DETERMINATION OF CARBON DISULPHIDE IN AIR

A-0. METHODS

A-0.1 Two methods, namely, Method A (Colorimetric) (**A-1**) and Method B (Volumetric) (**A-2**) are described.

A-1. METHOD A (COLORIMETRIC)

A-1.0 Outline of Method — The concentration of carbon disulphide in air may be determined colorimetrically after absorption in an *iso*butanol solution of diethanolamine and cupric acetate to form the golden-brown copper diethanol dithiocarbamate $[(C_2H_4OH)\ 2\ NCS_2]_2$ Cu. The intensity of colour is directly proportional to the concentration of carbon disulphide and is measured visually by comparison with known standards, or photometrically. With the photometric procedure, it is possible to detect concentrations of carbon disulphide as low as 1 ppm. Interfering substances, such as hydrogen sulphide and sulphur dioxide, are removed by absorption in alkaline cadmium chloride.

A-1.1 Reagents

A-1.1.1 *Alkaline Cadmium Chloride Solution* — containing 1.0 g cadmium chloride ($CdCl_2$, $2H_2O$) and 3.6 g sodium hydroxide (NaOH) per litre.

A-1.1.2 *Carbon Disulphide Reagent* — containing exactly 0.133 3 g analytical reagent grade cupric acetate $(CH_3COO)_2Cu$, H_2O and 200 ml technical grade diethanolamine per litre in *iso*butanol (boiling range 106 to 110°C).

A-1.2 Apparatus

A-1.2.1 *Standards* — for visual or photometric comparison.

A-1.2.1.1 *Visual standards* — to obtain stable standards for the visual comparison, solutions, containing no excess copper are prepared by adding a standard cupric acetate solution [0.152 8 g analytical reagent grade $(CH_3COO)_2$ Cu, H_2O and 5.0 ml diethylamine per litre in *iso*butanol] to a solution containing a large excess of carbon disulphide. Prepare a series of solutions containing various concentrations of copper diethyl dithiocarbamate by adding measured amounts of the acetate solution to sufficient 1 percent of carbon disulphide solution in *iso*butanol to make a total volume of 3 ml. Transfer the standard solution to 15 × 125 mm test-tubes, chill the tubes in an ice-salt mixture, and carefully seal off each tube. These standards are stable for about one month when protected from light and heat.

A-1.2.1.2 *Photometric standards* — Prepare a series of solutions containing various concentrations of copper diethanol dithiocarbamate by adding exactly to 1 ml portion of *iso*butanol containing known amounts of carbon disulphide to exactly 2 ml of carbon disulphide reagent solution [0.200 0 g analytical reagent grade $(CH_3COO)_2$ Cu, H_2O and 300 ml diethanolamine per litre in *iso*butanol]. Construct a calibration curve by plotting absorbance against concentration of carbon disulphide in milligrams.

A-1.2.2 *Sampling and Absorption Unit* — Fit each of the three 15 × 125 mm side-arm test-tubes with a length of glass tubing, drawn down to an orifice of 0.50 to 0.75 mm ID, and reaching the bottom of the tube. The test-tubes may be all glass filled with inlet and outlet tubes or the small tubes may be held through a rubber bung. Connect the tubes in series, with the side-arm of one attached to the inlet tube of the other, and connect the side-arm of the third tube to a sampling device capable of delivering a measured volume of air at any desired rate. A convenient sampler may be made by calibrating a double action short piston hand pump to deliver a measured volume of air with each stroke. Connect the side-arm of the second tube to the suction side of the pump through a trap.

A-1.2.3 *Photoelectric Photometer* — capable of giving good efficiency at 410 mμ (optional).

A-1.3 Procedure

A-1.3.1 Prepare the sampling and absorption unit by transferring 3 ml of the well-mixed alkaline cadmium chloride solution to the first side-arm test-tube and pipetting exactly 3 ml of the carbon disulphide reagent into the second and third tubes. Put the tubes in place and attach the sampling line (after flushing well with the air to be tested) to the inlet tube of the first test-tube so that the sample will pass first through the cadmium chloride solution and then through the carbon disulphide reagent tube.

A-1.3.2 Take the sample at a rate of about 300 ml per minute. When a definite golden-brown colour is visible in the carbon disulphide reagent tube, cut off the air flow and disconnect the tubes. Note the flowmeter reading. Allow the solutions to stand for at least 1 minute but not more than, 60 minutes, before measuring the intensity of the colour. Transfer the contents of second and third absorbers to a 100-ml volumetric flask after thorough rinsing with *iso*butanol and make up the volume with *iso*butanol.

A-1.3.3 Determine the concentration of carbon disulphide in the sample by measuring the absorbance at 410 mμ of the solution in the carbon disulphide reagent traps by means of a photoelectric photometer. Referring to the previously constructed calibration curve and determine milligrams of carbon disulphide present.

A-1.3.4 Alternatively, estimate the carbon disulphide concentration by visually comparing the solution with visual standards, using a white background for a light source and choosing the standard which compares most nearly with the sample.

A-1.4 Calculation

$$\text{Carbon disulphide in air, ppm } (v/v) = \frac{326\,W}{V}$$

where

W = mg of carbon disulphide, and

V = volume in litres of air passed.

A-2. METHOD B (VOLUMETRIC)

A-2.0 Outline of Method — Air is passed through five absorbers in series, the first three containing 2 percent cadmium chloride solution and the last two containing 5 percent alcoholic potassium hydroxide. Hydrogen sulphide is removed by absorption in alkaline cadmium chloride solution. Alcoholic potassium hydroxide solution absorbs carbon disulphide.

A-2.1 Reagents

A-2.1.1 *Cadmium Chloride Solution* — Dissolve 10 g of the cadmium chloride ($CdCl_2$) in 450 ml water to which is added to 10 ml of 0.5 N sodium hydroxide (NaOH) solution. Cadmium sulphate solution (5 percent) may also be used if chloride is not available.

A-2.1.2 *Standard Iodine Solution* — 0.005 N.

A-2.1.3 *Standard Sodium Thiosulphate Solution* — 0.005 N.

A-2.1.4 *Hydrochloric Acid* — concentrated.

A-2.1.5 *Alcoholic Potassium Hydroxide Solution* — Dissolve 5 g of potassium hydroxide (KOH) in 2 to 3 ml of water and dilute to 100 ml with absolute ethyl alcohol. This solution should be prepared fresh just before scrubbing the air.

A-2.1.6 *Starch Indicator* — Dissolve about 0.1 g in 25 ml of water. (should be freshly prepared).

A-2.1.7 *Acetic Acid* — 5 percent.

A-2.1.8 *Phenolphthalein Indicator* — 1 percent.

A-2.2 Procedure — Draw air through five absorbers in series, the first three each containing 30 ml of cadmium chloride solution and the last two absorbers each containing 30 ml of 5 percent alcoholic potassium hydroxide solution. Pass 8 litres of air at the rate of 0.5 litres per minute. Transfer the contents of last two scrubbers into a flask, rinsing the scrubbers with a little alcohol. Neutralize the solution with 5 percent acetic acid using phenolphthalein as an internal indicator. The acid solution should be added slowly and the sample is immersed in an ice-bath during the neutralization, to prevent any decomposition of the xanthate. Add starch indicator and titrate at once with 0.005 N iodine solution. For clear end point the solution should be cooled in ice-bath prior to titration. Afterwards the solution should be diluted 4 times with cooled distilled water to get a clear end point. Run a blank following the same precautions.

A-2.3 Calculation

$$\text{Carbon disulphide, ppm } (v/v) = \frac{24\ 800\ a\ N}{V}$$

where

a = millilitres of 0.005 N iodine solution consumed after correcting for blank

N = normality of iodine solution, and

V = litres of air passed.

NOTE 1 — Hydrogen sulphide may also be determined, if necessary, by oxidizing the content of cadmium chloride bubblers with standard iodine solution and titrating the excess with standard sodium thiosulphate solution.

NOTE 2 — Calculations (**A-1.4** and **A-2.3**) are based on the assumption that the temperature of air sample is 30°C and that the pressure is normal.

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